

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07C 2/06, 11/02, 29/16, 31/125, 303/24, 305/06, 51/16, 53/126, C11D 1/14		A1	(11) International Publication Number: WO 97/38957
			(43) International Publication Date: 23 October 1997 (23.10.97)
(21) International Application Number: PCT/US97/06485		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 16 April 1997 (16.04.97)			
(30) Priority Data: 60/015,521 16 April 1996 (16.04.96) US			
(71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).			
(72) Inventor; and			
(75) Inventor/Applicant (for US only): CONNOR, Daniel, Stedman [US/US]; 9217 Sagemeadow Drive, Cincinnati, OH 45251 (US).			
(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: BRANCHED SURFACTANT MANUFACTURE			
(57) Abstract			
<p>Alpha-olefins are dimerised to form vinylidene olefins, which are then isomerised and reacted with CO/H₂ under OXO conditions or reacted directly with CO/H₂ under OXO conditions to give mid- to near-mid chain branched alcohols. These branched-chain alcohols are feedstocks for the production of alkyl sulphate, alkyl ethoxy sulphate, and alkyl carboxylate surfactants and other surfactants.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LJ	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

BRANCHED SURFACTANT MANUFACTURE

FIELD OF THE INVENTION

5 The present invention relates to processes for manufacturing deterative surfactants, especially those containing branched-chain hydrophobic units.

BACKGROUND OF THE INVENTION

10 Conventional deterative surfactants comprise molecules having a water-solubilizing substituent (hydrophilic group) and an oleophilic substituent (hydrophobic group). Such surfactants typically comprise hydrophilic groups such as carboxylate, sulfate, sulfonate, amine oxide, polyoxyethylene, and the like, attached to an alkyl, alkenyl or alkaryl hydrophobe usually containing from about 10 to about 20 carbon atoms. Accordingly, the manufacturer of such surfactants must have access to a source of hydrophobe groups to which the desired hydrophile can be attached by chemical means. The earliest source of hydrophobe groups comprised the natural fats and oils, which were converted into soaps (i.e., carboxylate hydrophile) by saponification with base. Coconut oil and palm oil are still used to manufacture soap, as well as to manufacture the alkyl sulfate ("AS") class of surfactants. Other hydrophobes are available from petrochemicals, including alkylated benzene which is used to manufacture alkyl benzene sulfonate surfactants ("LAS").

15 The literature asserts that certain branched hydrophobes can be used to advantage in the manufacture of alkyl sulfate deterative surfactants; see, for example, U.S. 3,480,556 to deWitt, et al., November 25, 1969. However, it has been determined that the beta-branched surfactants described in the '556 patent are inferior with respect to certain solubility parameters, as evidenced by their Krafft temperatures. It has further been determined that surfactants having branching towards the center of carbon chain of the hydrophobe have much lower Krafft temperatures. See: "The Aqueous Phase Behavior of Surfactants", R.G. Laughlin, Academic Press, N.Y. (1994) p. 347. Accordingly, it has now been determined that such surfactants are preferred for use especially under cool or cold water washing conditions (e.g., 20°C-5°C).

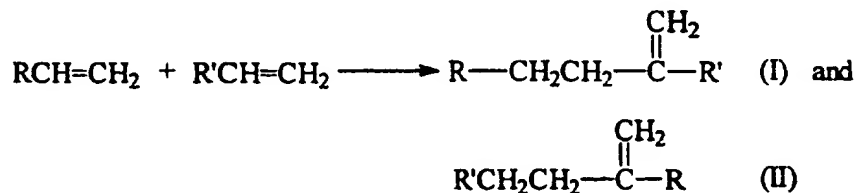
20 One problem associated with the manufacture of deterative surfactants having hydrophobe groups with mid- or near-mid chain branching is the lack of a ready source of such hydrophobes. By the present invention, a process is described for manufacturing such branched hydrophobes and converting them into mid- or near-mid chain branched surfactants.

SUMMARY OF THE INVENTION

The present invention encompasses a process for preparing mid- to near mid-chain branched olefins (primarily, methyl branched at or near the mid-chain region). Such materials are then used as the basic feedstock which provides the hydrophobic portion of branched-chain deterative surfactants.

The process herein is illustrated by the following reaction sequence.

1) Alpha-Olefin Dimerization



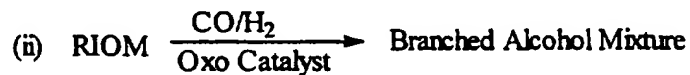
wherein R and R' may be the same or different linear alkyl, and

wherein R is C₃-C₇, preferably C₅ to C₇ linear alkyl, and R' is C₃-C₇, preferably C₅-C₇ linear alkyl. For use in preparing surfactants in cleaning products such as laundry detergents, dishwashing liquids, and the like, R and R' are preferably the same or within one or two carbon atoms of each other in chain length. Some linear olefins may also result from the dimerization and these can optionally be removed using molecular sieves. Step 1 of the process herein is designed to provide branched olefins which preferably contain from about 12 to about 18 (avg.) total carbon atoms.

2) Alcohol Production

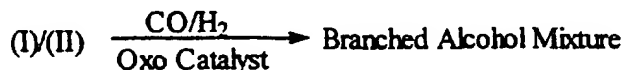
In Step 2 (Route A), the olefin mixture for Step 1 can be pre-randomized to enhance the ultimate formation of alcohols (i) and (ii) in subsequent Step 3. Alternatively (Step 2, Route B), this pre-randomization step can be deleted and the Oxo catalyst, itself, can randomize the final product among the three possible terminal positions.

Route A



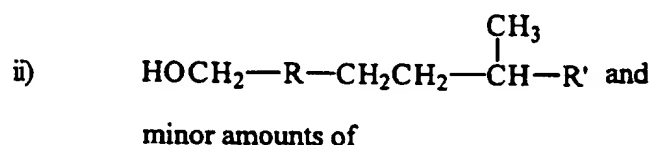
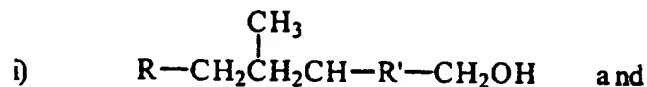
or

Route B



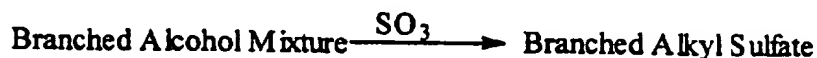
The Oxo process to make alcohols is described in detail in Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Volume 1, pp. 903-8 (1991), Jacqueline I. Kroschwitz, Executive Editor, Wiley-Interscience, N.Y. The catalyst for this step is, for example, cobalt-carbon monoxide-organophosphine.

- 5 The alcohol mixture of Step (2) of the present process comprises branched-chain primary alcohol compounds of the following formulae for use in Step (3), below.



- 10 It is to be understood that when CH₂OH is substituted on R or R' it is primarily on their respective terminal carbons or to a lesser extent on their penultimate carbons. Desirably, minimal amounts of compounds of the formula (iii) are present in Step (3).

3) Surfactant Production



- 15 Advantageously, the present process results in no geminal branching, i.e., no "quaternary" carbon substitution. Steric hindrance will block inverse addition to vinylidene carbon with cobalt-carbon monoxide-organophosphine which otherwise would form a non-biodegradable quaternary carbon. Moreover, little (less than about 3%) vicinal branching occurs. Of course, some of the overall feedstock may
- 20 remain unbranched. Typically, and preferably from the standpoint of cleaning performance and biodegradability, the present process provides hydrophobes with one near-central methyl in the case of isomers i) and ii).

- 25 All percentages, ratios and proportions herein are by weight, unless otherwise specified. All documents cited herein are, in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

1) Olefin dimerization:

The present invention encompasses, in a process for preparing surfactant precursor hydrophobes from dimerization of two same or near same chain length alpha-olefins to form a detergent range vinylidene olefin. These alpha olefins C₅ to C₁₀, preferably C₇ to C₉ are dimerized to give C₁₀ to C₂₀, preferably C₁₄ to C₁₈ vinylidene olefins which upon Oxo reaction give C₁₁ to C₂₁, preferably C₁₅ to C₁₉ alcohols. There are a number of processes for accomplishing said dimerization; see US Application 9,200,398, US 4,658,078, US 4,973,788; O. S. Vostrikova, A. G. Ibragimov, G. A. Tolstikov, L. M. Zelenova and U. M. Dzhemilev, Izv. Akad. Nauk SSSR, Ser. Khim. (1980), (10), 2330-2 [Chem. Abstr. 94:65032]; Jpn. Kokai Tokkyo Koho, 06228016 A2 [Chem. Abstr. 122:186930].

2) Alcohol Production

Route A

part a) The carbon-carbon double bond of the vinylidene olefin is pre-isomerized using a method such as Shell uses to isomerize alpha-olefins in their SHOP process; see Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Volume 17, pp. 848-50 (1996), Jacqueline I. Kroschwitz, Executive Editor, Wiley-Interscience, N. Y. and Chemical Economics Handbook, pp. 681.5030K-L, Stanford Research Institute, Menlo Park, CA 94025, Oct. 1993.

part b) Oxo chemistry is used to convert the pre-isomerized vinylidene olefin (now largely internal olefin) to a primary alcohol mixture. For this an Oxo catalyst which isomerizes the double bond to alpha positions prior to carbonylation is desired as is the case using cobalt-carbonyl-phosphine catalysts in the one step process, see Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Volume 1, pp. 903-8 (1991). Route A, (that is including pre-isomerization) is undertaken to assure relatively high yields of alcohols i and ii versus alcohol iii. Note alcohol sulfates of i and ii are desired surfactants whereas that of iii may be deficient.

Route B

This step utilizes the same Oxo catalyst on the vinylidene olefin directly without its pre-isomerization. This relies upon the catalyst to completely isomerize the carbon-carbon double bond of the vinylidene olefin prior to carbonylation. The object is to obtain as much i and ii relative to iii as is obtained in Route A.

Other fatty alcohol-derived surfactants can also be made, e.g., alkyl ethoxyl sulfates (AES), alkyl polyglucosides (APG), etc. Note that surfactants other than alcohol sulfates or AES may be made by oxidizing said alcohol or its aldehyde intermediate into a carboxylate (i.e., a branched-chain soap). This soap can be an excellent surfactant and/or detergent builder in and of itself. This carboxylate can also be used as a feedstock and converted to branched acyl-taurates, -isethionates, -

sarcosinates, -N-methylglucamide or other acyl-derived surfactants using art-disclosed techniques.

INDUSTRIAL APPLICABILITY

5 Branched-chain surfactants of the type resulting from the present process can be used in all manner of cleaning compositions. Such compositions include, but are not limited to: granular, bar-form and liquid laundry detergents; liquid hand dishwashing compositions; liquid, gel and bar-form personal cleansing products; shampoos; dentifrices; hard surface cleaners, and the like. Such compositions can contain a variety of conventional detergent ingredients. The following listing of
10 such ingredients is for the convenience of the formulator, and not by way of limitation of the types of ingredients which can be used with the branched-chain surfactants herein.

The branched-chain surfactants herein can be used in combination with detergent builders. Such builders include, for example, 1-10 micrometer zeolite A,
15 polycarboxylate builders such as citrate, layered silicate builders such as "SKS-6" (Hoechst) and phosphate materials, especially sodium tripolyphosphate ("STPP"). Most laundry detergents typically comprise at least about 1% builder, more typically from about 5% to about 80% builder or mixtures of builders.

Enzymes, such as proteases, amylases, lipases, cellulases, peroxidases, and
20 mixtures thereof, can be employed in detergent compositions containing the branched-chain surfactants. Typical detergent compositions comprise from about 0.001% to about 5% of commercial enzymes.

Detergent compositions can also contain polymeric soil release agents (SRA's). Such materials include, for example, anionic, cationic and non-charged
25 monomer units, especially polyester materials. Preferred materials of this type include oligomeric terephthalate esters, sulfonated substantially linear ester oligomers comprising a backbone of terephthaloyl and oxyalkyleneoxy repeat units and phthaloyl-derived sulfonated terminal moieties. A variety of SRA's are described, for example, in U.S. 4,968,451; 4,711,730; 4,721,580; 4,702,857;
30 4,877,896; 5,415,807; and in other literature references. Such soil release materials typically comprise from about 0.01% to about 10% of finished detergent compositions.

Detergent compositions may also optionally contain bleaching compositions comprising a bleaching agent and one or more bleach activators. If present,
35 bleaching agents such as percarbonate or perborate (especially perborate monohydrate "PB1") typically are used at levels from about 1% to about 30% of finished detergent compositions. Bleach activators such as nonanoyloxy-benzene

sulfonate ("NOBS") and tetraacetyl ethylenediamine ("TAED"), and mixtures thereof, can be used to enhance the bleaching activity of materials such as perborate and percarbonate. If present, the amount of bleach activator will typically be from about 0.1% to about 60% of a bleaching composition comprising a bleaching agent-
5 plus-bleach activator. Other bleaching agents such as the so-called "photoactivated" bleaches (see U.S. 4,033,718) can also be used. Sulfonated zinc phthalocyanine is an especially preferred photoactivated bleaching agent.

Detergent compositions can also contain clay soil removal/antiredeposition agents such as ethoxylated tetraethylene pentamine; see U.S. 4,597,898. Such
10 materials typically comprise from about 0.01% to about 10% of fully-formulated laundry detergents.

Detergent compositions can also contain from about 0.1% to about 7% of polymeric dispersing agents, which are especially useful in the presence of zeolite and/or layered silicate builders. Such materials are known in the art (see U.S.
15 3,308,067). Such materials include acrylate/malic-based copolymers, such as described in EP 193,360, as well as polyethylene glycol ("PEG").

Detergent compositions herein can also include various brighteners, dye transfer inhibiting agents (especially polymers of N-vinylpyrrolidone and N-vinylimidazole), suds suppressors (especially silicones), chelating agents such as
20 nitrilotriacetate, ethylenediamine disuccinate, and the like. Such materials will typically comprise from about 0.5% to about 10%, by weight, of fully-formulated cleaning compositions.

Moreover, it is to be understood that the branched-chain surfactants prepared in the manner of the present invention may be used singly in cleaning compositions
25 or in combination with other deterative surfactants. Typically, fully-formulated cleaning compositions will contain a mixture of surfactant types in order to obtain broad-scale cleaning performance over a variety of soils and stains and under a variety of usage conditions. One advantage of the branched-chain surfactants herein is their ability to be readily formulated in combination with other known surfactant
30 types. Nonlimiting examples of additional surfactants which may be used herein typically at levels from about 1% to about 55%, by weight, include the unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-18 glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides
35 and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. Nonionic surfactants such as the ethoxylated C₁₀-C₁₈ alcohols and alkyl phenols, (e.g., C₁₀-C₁₈ EO (1-10) can also be used. If desired, other

conventional surfactants such as the C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. C₁₀C₁₄ alkyl benzene sulfonates (LAS), which are often used in laundry detergent compositions, can also be used with the branched surfactants herein.

The following Examples illustrate the use of branched-chain surfactants prepared according to the present invention in various cleaning compositions, but is not intended to be limiting thereof.

15

EXAMPLE I

Granular laundry detergents are prepared as follows.

	<u>A</u>	<u>B</u>	<u>C</u>
Blown Powder			
Zeolite A	30.0	22.0	6.0
20 Sodium sulfate	19.0	5.0	7.0
Polyacrylate			
LAS	13.0	11.0	21.0
Branched AS*	9.0	8.0	8.0
Silicate, Na	-	1.0	5.0
25 Soap	-	-	2.0
Carbonate, Na	8.0	16.0	20.0
Spray On			
C ₁₄₋₁₅ EO7	1.0	1.0	1.0
Dry additives			
30 Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
NOBS	-	6.1	4.5
35 PB1	1.0	5.0	6.0
Sodium sulfate	-	6.0	-
Moisture & Miscellaneous	-----Balance-----		

*C₁₂-C₁₄ methyl branched alkyl sulfate, prepared as disclosed above.

A bleach-containing nonaqueous liquid laundry detergent is prepared as follows.

EXAMPLE II

5	<u>Component</u>	<u>Wt. %</u>	<u>Range (%)</u>
	<u>wt.)</u>		
	<u>Liquid Phase</u>		
	Branched AS*	25.3	18-35
	C ₁₂₋₁₄ , EO5 alcohol ethoxylate	13.6	10-20
10	Hexylene glycol	27.3	20-30
	Perfume	0.4	0-1.0
	<u>Solids</u>		
	Protease enzyme	0.4	0-1.0
	Na ₃ Citrate, anhydrous	4.3	3-6
15	Sodium perborate (PB-1)	3.4	2-7
	Sodium nonanoyloxybenzene sulfonate (NOBS)	8.0	2-12
	Sodium carbonate	13.9	5-20
	Diethyl triamine pentaacetic acid (DTPA)	0.9	0-1.5
	Brightener	0.4	0-0.6
20	Suds Suppressor	0.1	0-0.3
	Minors	-----Balance-----	

*C₁₂-C₁₆ methyl branched alkyl sulfate, Na salt, prepared as disclosed above.

A hand dishwashing liquid is as follows.

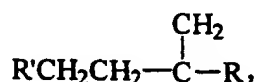
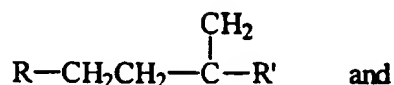
EXAMPLE III

	<u>Ingredient</u>	<u>% (wt.)</u>	<u>Range (% wt.)</u>
	Branched AS*	13.0	5-15
5	Ammonium C ₁₂₋₁₃ alkyl ethoxy sulfate	15.0	10-35
	Coconut amine oxide	2.6	2-5
	Betaine**/Tetronic 704®	0.87-0.10	0-2 (mix)
	Alcohol Ethoxylate C ₈ E ₁₁	5.0	2-10
10	Ammonium xylene sulfonate	4.0	1-6
	Ethanol	4.0	0-7
	Ammonium citrate	0.06	0-1.0
	Magnesium chloride	3.3	0-4.0
	Calcium chloride	2.5	0-4.0
15	Ammonium sulfate	0.08	0-4.0
	Hydrogen peroxide	200 ppm	0-300 ppm
	Perfume	0.18	0-0.5
	Maxatase® protease	0.50	0-1.0
	Water and minors	-----Balance-----	
20	*C ₁₂ C ₁₄ methyl branched alkyl sulfate, triethanolammonium salt, prepared as disclosed above.		
	**Cocoalkyl betaine.		

WHAT IS CLAIMED IS:

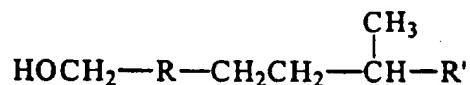
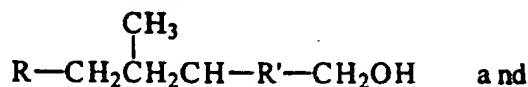
1. A process for preparing mid- to near-mid chain branched alcohols, comprising the steps of:

- (a) dimerizing alpha olefins of the formula $RCH=CH_2$ and $R'CH_2=CH_2$, to form olefins of the formula:



wherein in the above formulas R and R' may be the same or different C_3 to C_7 linear alkyl substituents; followed by either

- (b) isomerizing the olefins from Step (a) and the subsequent reaction of said isomerized olefins with CO/H_2 under Oxo conditions; or directly reacting the olefins from Step (a) with CO/H_2 under Oxo conditions; and
- (c) recovering the desired branched alcohols of the formula:



2. A process for preparing branched alkyl sulfate surfactants by sulfating the alcohols prepared according to Claim 1.

3. A process for preparing branched alkyl ethoxy sulfates, comprising first ethoxylating, then sulfating, the alcohols prepared according to Claim 1.

4. A process for preparing branched alkyl carboxylate surfactants by oxidizing the alcohols prepared according to Claim 1, or their aldehyde intermediates.

5. A process for preparing branched acyl taurate, branched acyl isethionate, branched acyl sarcosinate, or branched acyl N-methylglucamine surfactants, or the like, using the branched carboxylates prepared according to Claim 4 as a feedstock.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/06485

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C2/06 C07C11/02 C07C29/16 C07C31/125 C07C303/24
C07C305/06 C07C51/16 C07C53/126 C11D1/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 446 213 A (K. SATO, ET AL.) 29 August 1995 see column 12, line 66 - column 14, line 9; claim 16; example 22 & JP 06 228 016 A (MITSUBISHI CHEM. IND.) cited in the application ---	1
A	US 2 695 327 A (K. ZIEGLER, ET AL.) 23 November 1954 see the whole document ---	1
A	US 3 647 906 A (F.F. FARLEY) 7 March 1972 see the whole document ---	1
A	US 3 480 556 A (W.J. DE WITT, ET AL.) 25 November 1969 cited in the application see the whole document ---	2,3
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

18 August 1997

Date of mailing of the international search report

2 5. 08. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

English, R

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/06485

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 401 642 A (HENKEL) 12 December 1990 see the whole document -----	2,3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/06485

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5446213 A	29-08-95	JP 6228016 A	16-08-94
US 2695327 A	23-11-54	NONE	
US 3647906 A	07-03-72	NONE	
US 3480556 A	25-11-69	NONE	
EP 401642 A	12-12-90	DE 3918252 A	13-12-90
		WO 9015049 A	13-12-90
		EP 0475967 A	25-03-92
		JP 4505916 T	15-10-92